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Synthetic Organic Chemicals

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Non-Aqueous Solutions

NON-AQUEOUS solvents have interested in turn the organic and the physical chemist. At the present time, this field has been largely absorbed by the latter, whose many and varied papers on the subject have apparently created an impression that all but the physical chemists have neglected the non-aqueous field. As a result, it is the opinion of many that a study of the nature and type of the reactions and products has been neglected for work on the physical constants.

However, it should be remembered that some of the classic reactions of organic chemistry are carried out in non-aqueous media. Excellent examples are the Claisen reaction, the Wurtz and Fittig syntheses, the Friedel and Crafts synthesis, and Grignard's reaction. These were studied specifically from the standpoint of products formed, especially the principal products. The mechanism of the Wurtz synthesis was elucidated by Clarke and Bachmann in J.A.C.S. *49*, 2089 (1927), who showed that free radicals must be present to account for some of the by-products. Gilman at Iowa State College, and Johnson at Cornell University have made many and valuable contributions based on Grignard's reaction.

Professor Nieuwland at Notre Dame is well known for his condensations of acetylene in non-aqueous media, and he has also found liquid ammonia ideal for some analytical and synthetic methods.

Liquid sulfur dioxide is used commercially as a solvent in the esterification of cellulose, as is glacial acetic acid, while a long list of non-aqueous substances, mainly hydrocarbons which are non-solvents for cellulose acetate, have been proposed for use in preparing this very valuable ester in fibrous form.

As early as 1834, Mitscherlich, in Ann. *12*, 311, described the reduction of aromatic nitro compounds with sodium alcoholate in anhydrous alcohol. Numerous investigators have since carried forward these researches. Dains and his students at the University of Kansas obtained interesting and unexpected results when reducing with alkali alcoholates in benzene. These are given in J.A.C.S. *53*, 2357 (1931).

Kraus of Brown University reduces with solutions of metals in liquid ammonia, J.A.C.S. *52*, 4432 (1930). Burgess of Cincinnati and his coworkers have studied the action of sodium on salts in liquid ammonia and have found that the metals reduced in this way are almost always very reactive toward air or water. Copper becomes incandescent, manganese sparks vigorously and becomes white-hot. Nickel behaves similarly, while sodium zinc reacts with explosive violence. Silver is the only exception; it appears to be non-reactive.

Electrodeposition of metals from various non-aqueous solvents has been

studied by many investigators, both here and abroad; and, while the literature is fragmentary, some of the results are of considerable interest and may eventually prove to be of commercial importance. Many substances, such as the alkali metals, have been successfully plated under anhydrous conditions, and metallic coatings or mercury amalgams of them obtained.

Some of the early investigations of Franklin and his students at Stanford University indicated that ammonium salts in liquid ammonia acted as acids, and more recently it has been observed that acetates in glacial acetic acid act as bases. The work of Conant and Hall focused the attention of the chemical world on the "Superacidity" of strong acids in organic solvents, and it appeared for a time that the strengths of acids might be measured by absolute hydrogen ion activity. However, Taylor and Guggenheim argue: "The electric potential difference between two points is a conception without any physical significance unless the two points are in the same media." If this view is accepted, Hall concludes: "The notion of absolute acidity, as distinct from the relative activities of some particular acid in two different solutions, must be relegated to the limbo of seductive but meaningless fiction."

The researches of Claisen, Wurtz, Fittig, Friedel and Crafts, Grignard, and the rest of those patriarchs of organic chemistry who worked in non-aqueous solvents ended in results which were neither fictitious nor meaningless. Their spirits still lend encouragement to present-day research.

Eastman Organic Chemicals as Analytical Reagents

XXXI MANGANESE

BENZIDINE HYDROCHLORIDE

Stratton, Ficklen, and Hough, IND. AND ENG. CHEM. (ANAL. ED.) *4*, 2 (1932)

The addition of benzidine hydrochloride to potassium permanganate solutions forms a bright blue-green color. In very dilute solutions this color is easier to estimate in the colorimeter than the permanganate color itself. Quantities as small as 0.0001 mg. permanganate in 100 c.c. yield a transient blue color which is matched with standards of copper sulfate and picric acid.

POTASSIUM PERIODATE

Clark, IND. AND ENG. CHEM. (ANAL. ED.) *5*, 241 (1933)

The potassium periodate method of Willard and Greathouse is found to be very satisfactory for manganese, especially if phosphoric acid is used as the acidifying agent. In analyzing salt solutions, the oxidations are made in 50 to 100 c.c. of a solution containing 5 c.c. of 85% phosphoric acid and 0.3 gram of potassium periodate. By a few minutes' boiling a permanent permanganate color is developed which can be compared in a Nessler tube against standards treated in the same manner.

TETRAMETHYLDIAMINO-DIPHENYLMETHANE

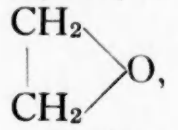
Trillat, COMPT. REND. *136*, 1205 (1903)

In acetic acid solution this reagent gives a deep blue color with lead and manganese dioxide. Five grams of the base are dissolved in 100 c.c. of water and 10 c.c. of acetic acid to form the reagent solution. The suspected substance is treated with sodium hydroxide and incinerated. The ash is moistened with acetic acid and then warmed with the reagent. If manganese is present, a blue color is developed. The presence of copper should be avoided.

Ethylene Oxide and Some of Its Reactions

ETHYLENE OXIDE has been known for a long time and due to its great reactivity has received considerable academic attention. However, its increasing commercial application makes it a compound of more than passing interest to the industrial chemist.

The compound, ethylene oxide



is obtained by distilling glycol chlorhydrin with caustic potash. It is also prepared commercially by forcing ethylenechlorhydrin and steam through a tower against a counter current of crude chlorhydrin. Still another method is to pass ethylenechlorhydrin over magnesium oxide heated to 250° C.

Ethylene oxide is characterized by its additive power; the formation of additive compounds being accompanied by rupture of the ring. The following is a list of some of its interesting reactions:

Ethylene oxide combines with water slowly and yields glycol.

Nascent hydrogen converts it into ethyl alcohol.

Halogen acids, except hydrogen fluoride, unite with it to form halogen hydrins (monohaloid esters of the glycols).

It reacts with ethyl alcohol to yield glycolmonoethyl ether.

With glycol it forms diethylene glycol.

With the latter (diethylene glycol) it combines to form triethylene glycol.

Ethylene oxide forms ethylene alkylidene ethers with aldehydes.

Acetic acid and ethylene oxide react to form glycol monoacetate.

With acetic anhydride the resulting product is glycol diacetate.

When ethylene oxide is allowed to react with sodium bisulfite, sodium isethionate is formed.

With hydrocyanic acid it forms the nitrile of ethylene lactic acid or hydracrylic acid which, upon hydrolysis with hydrochloric acid, yields the ethylene lactic acid itself.

Ammonia changes ethylene oxide to hydroxyethylamine.

Ethylene oxide and magnesium alkyl halides react to form addition compounds which may then be converted by heat into primary alcoholates, RCH_2CH_2OMgX.

When ethylene oxide is heated to 380°-444° C. in a pyrex chamber, it decomposes. The final products are carbon monoxide and methane.

Ethylene oxide forms hydrazine alcohols with hydrazine.

With thioureas, ethylene oxide reacts to form more or less stable thio ethers or their hydrolysis products.

Aldehydes are formed when ethylene oxide in vapor form is passed over catalysts, for example, magnesium pyrophosphate mixed with kieselguhr.

By the action of a solution of ethylene oxide in acetone on mercerized cellulose, a cellulose hydroxyethyl ether has been obtained. A triacetate has been formed by acetylating the ether with acetic anhydride and sulfuric acid.

This is of necessity but a partial list of the many reactions of ethylene oxide. Further researches on the properties and applications of this interesting compound will undoubtedly increase its already important place in industrial usage.

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If you wish to continue receiving "Synthetic Organic Chemicals" be sure to fill in and mail the post card accompanying this issue.

We are revising the mailing list and your reply is necessary.

New Eastman Organic Chemicals

The following chemicals have recently been added to our list:

P 3604	iso-Butyl Lactate (Practical) BP 67-73°/15 mm.	100 g.	$4.25 C
P 3602	tert.-Butyl Mercaptan (Practical) BP 62-72°	500 g.	9.50 D
69	Chloroacetyl Chloride BP 105-106°	500 g.	4.50 D
3605	α-Chloropropionic Acid BP 82-84°/15 mm.	500 g.	6.00 D
3603	2,3-Dichlorodioxane BP 88-89°/19 mm.	100 g.	3.00 C
P 3471	Disodium 2,6-Dibromobenzenoneindo-3′-carboxyphenol (Practical)	1 g.	1.00 A
3097	Epinephrine	1 g.	4.00 O
3600	Ethyl Pimelate BP 142-145°/15 mm.	10 g.	2.00 A
P 3601	4-Nitro-2-aminoanisole (Practical) MP 116-118°	500 g.	9.50 D
2617	4-Nitroguaiacol MP 103-105°	10 g.	4.00 A
3472	Pimelic Acid MP 103-104°	10 g.	3.50 A
P 3487	Sodium Benzenoneindophenol (Practical)	1 g.	1.00 A
P 3489	Sodium 2-Chlorobenzenoneindophenol (Practical)	1 g.	1.00 A
P 3468	Sodium 2,6-Dibromobenzenoneindo-2′-bromophenol (Practical)	1 g.	1.00 A
P 3456	Sodium 2,6-Dibromobenzenoneindo-3′-bromophenol (Practical)	1 g.	1.00 A
P 3470	Sodium 2,6-Dibromobenzenoneindo-3′-methoxyphenol (Practical)	1 g.	1.00 A
P 3469	Sodium 2,6-Dibromobenzenoneindo-3′-methylphenol (Practical)	1 g.	1.00 A
P 3531	Sodium 2,6-Dibromobenzenoneindophenol (Practical)	1 g.	1.00 A
P 3500	Sodium 2,6-Dibromobenzenone-2′-methyl-5′-iso-propylindophenol (Practical)	1 g.	1.00 A
P 3467	Sodium 2,6-Dichlorobenzenoneindo-3′-chlorophenol (Practical)	1 g.	1.00 A
P 3466	Sodium 2,6-Dichlorobenzenoneindo-3′-methylphenol (Practical)	1 g.	1.00 A
P 3463	Sodium 2,6-Dichlorobenzenoneindophenol (Practical)	1 g.	1.00 A
P 3488	Sodium 2-Methylbenzenoneindophenol (Practical)	1 g.	1.00 A
P 3505	Sodium 2-Methyl-5-iso-propylbenzenoneindophenol (Practical)	1 g.	1.00 A
P 3499	Sodium 3-Methyl-6-iso-propylbenzenoneindophenol (Practical)	1 g.	1.00 A
P 3597	Sodium Tetrahydronaphthalene-beta-sulfonate (Practical)	100 g.	3.50 C